

MANGANESE DIOXIDE FOR LITHIUM BATTERY CATHODES

The present invention relates to chemical power sources, and in particular to chemical power sources with lithium anode and non-aqueous electrolyte, in which manganese dioxide is used as an active cathode substance, with the objective of developing manganese dioxide to provide high efficiency for both primary and secondary Li-MnO₂ cells.

In order to provide highly efficient and highly stable electrochemical characteristics for cathodes of lithium batteries based on MnO₂, the MnO₂ must have specific properties. These properties can be achieved by using special processes for synthesis. As a result, the power sources based on this oxide would have desirable characteristics in both primary and rechargeable product applications.

Manganese dioxide for lithium power sources with a primary discharge capacity of 140mAh/g (in terms of cathode substance) have been described. This capacity drops to 90.0 mA·h/g in the 300th cycle (A 3 volt lithium manganese oxide cathode for rechargeable lithium batteries/Huang Haitao, Bruce Peter G., J. Electrochem. Soc.-1994/-141. #7.-CL76-L77).

A manganese dioxide with the discharge capacity during the first discharge of 150mAh/g has also been reported. During repeated cycling the discharge capacity decreases below the 90.0 mAh/g (Investigation of lithiated manganese oxides as the materials for rechargeable cathode of lithium chemical power sources», N.I.Globa, E.M.Shembel, A.S. Strizhko. Abstract. The 3d Meeting on lithium power sources, Ekaterinobourg, October 4-7, 1994.- P.6).

The low discharge capacity of the MnO₂ based cathode for the first discharge process and the characteristic instability of Li-MnO₂ power sources during cycling are the disadvantages of the above mentioned MnO₂ materials. .

The electrochemical method of manganese dioxide synthesis from electrolyte based on water solution has been described. During electrochemical synthesis the MnO_2 is deposited on the anode surface. Manganese dioxide that is produced by the method of electrochemical synthesis is used as a cathode material in the different types of the chemical power sources: a) with none aqueous electrolyte and lithium anode; b) salt based aqueous electrolyte and a zinc based anode; c) alkaline based electrolytes and a zinc-based anode.

The main disadvantage of electrochemically synthesized manganese dioxide is its low tap density. As a result of the low tap density, cathodes based on electrochemically synthesized manganese dioxide have low specific discharge characteristics per volume, expressed in mAh/cm^3 . As a result, the chemical power sources, which utilize cathodes based on electrochemically synthesized manganese dioxide, also have the low discharge characteristics on a per-volume basis.

The method of chemical synthesis for manganese dioxide is based on manganese nitrate oxidation by sodium chlorate in 30-32%- nitric acid at $85-90^\circ\text{C}$ followed by separation, washing and drying of the product deposit at $105-110^\circ\text{C}$. (Patent of FSU (USSR) № 1347353 of 10.09.85; MKI CO1G 45/02) is the closest to that of the present invention.

Disadvantages of MnO_2 produced by the methods mentioned above are as follows:

- non- serviceability in lithium power sources due to the crystallization moisture up to 5%, which is not removed under common conditions of treatment.
- low concentration of MnO_2 active substance (90-92) %
- low bulk density of the product; not more than $2.3-2.4 \text{ kg/dm}^3$
- low conductivity of the product, equal to not more than 3.0 S/m (conductivity has been determined by the non-contact eddy-current method according US Patent Application 11/244,796).

An objective of the present invention is to improve the quality of the manganese dioxide and provide manganese oxide powder with high tap density and high electronic conductivity, as well as high discharge capacity and more efficient cycling characteristics.

This objective is achieved in that the manganese dioxide of the present invention for the cathodes of lithium power sources is produced by manganese nitrate oxidation by sodium chlorate in a nitric acid medium. Oxidation is provided by heating followed by separation from the reaction mixture. After separation, the oxide is thermally treated. According to the invention, the nitric acid concentration during the MnO_2 synthesis is changed from 38-44% at the beginning and up to 23-26% at the end of the synthesis process. After the synthesis, thermal treatment of the product is carried out in air at 240-320°C. The structure of manganese oxide is characterized by the formation in the x-ray phase mixture of the γ and the β phases.

The manganese dioxide produced based on the synthesis method described in the current invention has considerable advantages as compared with known prior manganese dioxide. Due the special condition of the synthesis, including:

the change the nitric acid concentration during the synthesis from 38-44% at the beginning and up to 23-26% at the end of the synthesis process, and special regime for treatment of the oxide in air at 240-320°C after synthesis.

The resulting manganese oxide has properties that favorably influence its electrochemical characteristics.

Manganese dioxide synthesized according this method has a bulk density of 2.5-2.9 kg/dm³ with integral particle distribution in the range 1-3 up to 60-70 μm . The ratio between a bulk density (in kg/L²) and specific surface (m²/g) of manganese dioxide is in the range of 0.08 – 0.40. The quantity of the pure total mass of MnO_2 in the oxide is 94.0-96.0%. The structure of the manganese oxide corresponds to the formation of the x-ray phase mixture of

the γ and the β phases. The effective electronic conductivity of the MnO_2 powder synthesized according the present invention is at least 3.4 S/m. Conductivity has been measured using the eddy-current non-contact testing at the frequency 120kHz (US Patent Application 11/244,796).

The density of the cathode mass based on manganese dioxide synthesized according the present invention is 2.7 – 2.9 g/ cm³. In non-aqueous electrolyte, the cathode discharge capacity at the first discharge is 270 mA·h/g in terms of the manganese dioxide. Upon cycling, the average discharge capacity is up to 170 mA·h/g.

Described below are the reasons why the characteristic of the manganese oxide of the current invention is important. The excellent characteristics of the manganese oxide synthesized according the method of current invention, and characteristic of cathodes based on this manganese oxide characteristics are determined by the following:

For manganese dioxide bulk density of less than 2.5 kg/dm³ and the ratio between bulk density and specific surface less than 0.08, the following negative effects are evident:

1. For manganese dioxide bulk density of less than 2.5 kg/dm³ and the ratio between bulk density and specific surface less than 0.08, the following negative effects are evident:

- cathode mass has the low level of the density (less than 2.0 kg/dm³), the structure of the manganese oxide powder affects the macrostructure of electrode. As a result, the electrode macrostructure is formed in such a way that primary discharge capacity is low. With such electrode macrostructure it is also impossible to achieve an effective charge process. As a result, the cycling of the power source is not practical. That is, the resulting microstructure leads to a sharp decrease in discharge capacity during cycling.

2. For manganese dioxide bulk density of greater than 2.9 kg/dm³, and the ratio between a bulk density and specific surface greater than 0.4, the following negative effects are evident:

- cathode mass is slightly granulated thus preventing the fabrication of high-quality cathodes.

3. When the fraction of total mass of manganese dioxide is less than 94% and conductivity less than 3.4 S/m, the following negative effects show themselves because of insufficient removal of crystallization moisture from a product and the primary prevalence of γ -MnO₂:

- primary discharge capacity of cathode decreases;
- cathode cyclability decreases sharply;
- discharge voltage value decreases.

4. When the fraction of manganese dioxide total mass is more than 96% the following negative effects, due to product transition into the passive β -MnO₂ structures, take place :

- primary discharge capacity of cathode decreases,
- sharp drop of cyclability occurs.

The synthesis method for manganese dioxide of the present invention changes the nitric acid concentration from 38-44% at the beginning of the synthesis process up to 23-26% at the end. The subsequent mode of thermal treatment enables production of manganese dioxide powder with an integral set of the particles from 1-3 up to 60-70 μ m. The ratio between a bulk density in (kg/dm³) and manganese dioxide specific surface (m²/g) is in the range of 0.08-0.40. The concentration of manganese dioxide is 94-96%, with the efficient conductivity of manganese dioxide powder as measured by an eddy-current method at a frequency of 120 MHz, of at least 3.4 S/m. This provides good discharge characteristics of batteries made with cathodes based on this material. To more clearly describe the present inventions, the following specific examples are provided.

Example 1.

0.4-0.8 dm³ of 38-44% nitric acid is placed into titanium reactor with the volume up to 1 dm³ overflow with a mechanical agitator. The manganese nitrate solutions are measured at 80-100°C. A reaction mixture comprising solid manganese dioxide is removed through the overflow into a separate container and filtered. The process is carried out until the nitric acid concentration in the reaction mixture is equal to 23-26%. The filtered product is washed to neutralize nitric acid residue, and dried at 105-140°C. In this case, bulk density of the produced powder is 2.5-2.9 kg/dm³ with the integral particle distribution ranging from 1-3 up to 60-70 µm.

Example 2.

Manganese dioxide, as produced in Example 1, was then thermally treated at 240-320°C until the manganese dioxide content was 94-96%. In this case, the powder form conductivity, as measured by the method of eddy-current at a frequency of 120 MHz (MPK7 G01N 27/02, 27/06, 27/22 № 54354A published 17.02.03. Bull. № 2) is at least 3.4 Sm/m.

Example 3.

Manganese dioxide powder as produced above is mixed with a conducting additive as a mixture of carbon black and graphite. The binder PTFE or PVdF is added to the slurry. The resulting cathode mass is deposited onto a stainless steel, aluminum or titanium grid or foil. The resulting cathode mass density is 2.7-2.9 g/cm³.

The resulting cathode can be used in primary and secondary lithium power sources. This is illustrated by the example below.

Example 4.

After drying, the cathode produced in accordance with the Example 3 is placed into non-aqueous electrolyte, where cathodes are tested and discharge capacity and discharge voltage are measured. The measurements are carried out in a three-electrode cell, where the investigated electrode based on manganese dioxide is used as a working electrode, and

lithium electrodes serve as auxiliary and reference electrodes. During cathode discharging, the capacity at the first cycle is 270 mAh/g. For the second and subsequent 80 discharge cycles, discharge capacity ranges from 170 to 145mAh/g.

Data from these examples are summarized by the results shown in Tables 1 and 2 below:

Table 1.

№	Bulk density of MnO_2	Relation between bulk density and specific surface	Fraction of MnO_2 total mass (%)	Conductivity (S/m)	HNO ₃ concentration at synthesis		Discharge cathode capacity, mAh/g (in terms of MnO_2)				Note
					initial	final	1 st cycle	2 nd cycle	10 th cycle	100 th cycle	
1	2	3	4	5	6	7	8	9	10	11	12
1	2.5	0.32	95	3.5	44	23	260	170	160	145	Claimed manganese dioxide properties
2	2.7	0.12	95	3.5	42	25	270	190	170	155	The same
3	2.9	0.26	95	3.5	41	25	255	160	150	145	The same
4	2.4	0.21	95	3.5	42	24	220	110	90	75	Low discharge capacity; bulk density of the product is lower than the claimed limit
5	3.0	0.09	95	3.5	43	25	210	110	90	70	Low discharge capacity; bulk density of the product is higher than the claimed limit
6	2.7	0.07	95	3.5	43	25	225	120	100	90	Low discharge capacity; ratio between bulk density and specific surface is lower than the claimed limit
7	2.7	.5	95	3.5	40	24	215	105	90	70	Low discharge capacity; ratio between bulk density and specific surface is higher than the claimed limit

Continuation of Table 1.

8	2.7	0.4	95	3.5	40	24	260	160	160	145	Claimed properties of manganese dioxide
9	2.7	0.31	96	3.5	42	25	250	155	155	145	The same
10	2.8	0.36	97	3.5	41	25	210	110	95	75	Low discharge capacity; high fraction of MnO ₂ total mass in a product
11	2.9	0.38	94	3.5	42	24	250	160	155	140	The being claimed properties of manganese dioxide
12	2.8	0.16	93	3.5	41	24	205	105	80	65	Low discharge capacity ; low fraction of MnO ₂ total mass in a product
13	2.8	0.22	95	3.5	40	24	240	160	145	140	The being claimed properties of manganese dioxide
14	2.7	0.23	95	3.3	44	24	210	110	95	75	Low discharge capacity; conductivity is lower than the claimed limit
15	2.9	0.38	95	3.5	45	27	220	125	100	95	Low discharge capacity; at the beginning and at the end of synthesis HNO ₃ concentration is higher than at the claimed limit.
16	2.5	0.09	95	3.5	37	22	210	110	95	75	Low discharge capacity; HNO ₃ concentration at the beginning and the end of a synthesis is lower than the being claimed limit

TABLE 2

Temperature of thermal treatment	X-ray phase composition	Manganese dioxide content (%)	Specific capacity of the 1 st cycle, mAh/g	Specific capacity at cycling, mAh/g
200	γ - MnO ₂	94	240	150
250	γ , β - MnO ₂	95	270	180
300	γ , β - MnO ₂	95	270	180
350	β - MnO ₂	94	230	120

As illustrated in the above examples and data tables, manganese dioxide with the characteristics described enables production of the cathodes with excellent discharge characteristics in both the primary and rechargeable lithium chemical power source with non-aqueous electrolyte